(12) UK Patent Application (19) GB (11) 2 107 325 A

(21) Application No 8224302
(22) Date of filing 24 Aug 1982
(30) Priority data
(31) 309561
(32) 8 Oct 1981
(33) United States of America (US)
(43) Application published 27 Apr 1983
(51) INT CL[3] C08L 23/00 53/00//B32B 27/04 27/28 27/32 31/30 C09J 3/14
(52) Domestic classification C3M 127 127AC 130 131 131C 133 134 139 139C 142 143 143A 146A 203 XC B5N 2704 2706 2710 2728 2730 2732 2734 3130 U1S 1369 1370 1591 C3M
(56) Documents cited
GB A 2045776
GB 1566495
GB 1566460
GB 1094820
EP A 0027375A
US 4198327
US 4087587
(58) Field of search
C3M
C3V
C3K
C3J

(71) Applicants
ACC Chemical Company, (USA—Delaware), 915 Harger Road, Oak Brook, Illinois, United States of America,
Getty Chemical Company, (USA—Delaware), 3810 Wilshire Boulevard, Los Angeles, California, United States of America
(72) Inventors
Seymour Schmukler,
John Machonis,
Mitsuzo Shida
(74) Agents
A. A. Thornton and Co., Northumberland House, 303/306 High Holborn, London, WC1V 7LE

(54) Composite structures of polypropylene and polar substrates

(57) Composite structures comprising polypropylene, a polar substrate and an adhesive blend securing them together are made with a blend which is essentially free of polypropylene and which comprises a polyethylene backbone polymer grafted with an unsaturated carboxylic acid or acid anhydride, an elastomer, and a polyolefin resin.

GB 2 107 325 A

SPECIFICATION

Composite structures and method of making same

This invention is concerned with composite structures comprising polypropylene and a polar polymer or metal, and with a method of making them.

Polypropylene is usually adhered to polar polymers, such as nylon, ethylene-vinyl alcohol copolymers (EVOH) and polyvinyl alcohol, and to metals, such as aluminium, steel, copper, tin and brass, by interposing a blend comprising polypropylene grafted with an unsaturated carboxylic acid or derivative thereof, and polypropylene. This blend is used directly as an adhesive layer between the polypropylene and the polar substrate.

It would be desirable to be able to use polyethylene grafted with an unsaturated carboxylic acid or derivative thereof because such graft copolymers can be readily prepared in a melt reaction system. If a blend of such a polyethylene graft copolymer with polypropylene is used, however, relatively poor adhesion is obtained to polar polymers and other polar substrates and, in some cases, no adhesion at all.

We have now found, however, that by using an adhesive blend comprising such a graft polyethylene copolymer, an elastomer, and an ethylene homopolymer or copolymer, excellent adhesion is obtained to both polypropylene and various substrates including polar polymers, metals, glass, paper, and wood. The elastomer promotes adhesion of the blend to polypropylene since without it, poor adhesion to polypropylene is obtained. This result could not have been predicted from the state of the art and is, therefore, surprising.

According to the present invention, there is provided a composite structure comprising a polypropylene structure, a solid substrate and sandwiched therebetween, an adhesive blend comprising:

(a) from 0.1 to 95% by weight of a graft copolymer of from 70 to 99.999% by weight of a polyethylene backbone grafted with from 30 to 0.001% by weight of an unsaturated carboxylic acid or acid anhydride thereof,

(b) at least one elastomer which is a homopolymer or copolymer of isobutylene, a homopolymer of chloroprene, an elastomeric copolymer of ethylene and an α-olefin, a terpolymer of ethylene, an α-olefin and a diene, a random or block copolymer of a diene and a vinyl aromatic compound, a copolymer of a hydrogenated diene and a vinyl aromatic compound, a hydrogenated block copolymer of a diene and a vinyl aromatic compound, a butadiene homopolymer, chlorinated butyl rubber, neoprene, a styrene-ethylene-butylene-styrene block copolymer, or a copolymer of an ethylenically unsaturated nitrile and a diene, and

(c) an ethylene homopolymer and/or a copolymer of ethylene and an α-olefin.

The polyethylene used as the backbone polymer for the graft copolymer forming component (a) of the adhesive blend is an ethylene homopolymer or a copolymer of ethylene with an α-olefin, such as propylene or butene-1. The polyethylene used for this purpose is preferably a linear polymer. Mixtures of two or more such homopolymers or copolymers can be used, if desired.

Suitable unsaturated carboxylic acids or acid derivatives for use as the grafting monomer in component (a) include, for example, acrylic acid, fumaric acid, methacrylic acid, maleic acid, itaconic acid, citraconic acid, mesaconic acid, maleic anhydride, citroconic anhydride, itaconic anhydride, 4-methyl cyclohex-4-ene-1,2-dicarboxylic acid anhydride, bicyclo(2.2.2)oct-5-ene-2,3-dicarboxylic acid anhydride, 1,2,3,4,5,8,9,10-octahydronaphthalene-2,2-dicarboxylic acid anhydride, 2-oxa-1,3-diketospiro(4,4)non-7-ene, bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic anhydride, maleo-pimaric acid, tetrahydrophthalic anhydride, x-methylnorborn-5-ene-2,3-dicarboxylic acid anhydride, norborn-5-ene-2,3-dicarboxylic acid anhydride, Nadic anhydride, methyl Nadic anhydride, Himic anhydride, methyl Himic anhydride and other fused ring monomers as described in U.S. Patents 3,873,643 and 3,882,194. Cograft copolymers as described in the latter U.S. patent can also be used as component (a).

Suitable elastomers to constitute component (b) of the adhesive blend include, for example, copolymers of isobutylene and isoprene, chlorinated copolymers of isobutylene and isoprene, copolymers of butadiene and styrene, copolymers of butadiene and vinyl toluene, block copolymers of butadiene and styrene, block copolymers of butadiene and vinyl toluene, block copolymers of isoprene and styrene, block copolymers of isoprene and vinyl toluene, hydrogenated copolymers of butadiene and styrene, hydrogenated block copolymers of butadiene and styrene, hydrogenated block copolymers of isoprene and styrene, styrene-ethylene-butylene-styrene block copolymers, copolymers of acrylonitrile and butadiene, copolymers of methacrylonitrile and butadiene, copolymers of acrylonitrile and isoprene, and copolymers of methacrylonitrile and isoprene.

Particularly preferred elastomers for use according to the invention include ethylene-propylene copolymers, ethylene-propylene-diene terpolymers, homopolymers of isobutylene, chlorinated copolymers of isobutylene and isoprene, homopolymers of chloroprene, hydrogenated block copolymers of styrene and butadiene, and styrene-ethylene-butylene-styrene block copolymers.

Suitable ethylene copolymers for use as component (c) of the adhesive blend are, for example,

copolymers of ethylene and propylene, butene-1 or hexene-1. Mixtures of two or more ethylene homopolymers or copolymers can be used, if desired.

The ethylene homopolymers or copolymers used as component (c) may be prepared by any convenient process using transition metal catalysts with low or medium pressure or radical initiators with high pressure. The polymers may be branched or linear low density polyethylenes, or medium or high density polyethylenes.

Examples of composite structures according to the invention are polypropylene/adhesive blend nylon, polypropylene/adhesive blend/ethylene-vinyl alcohol copolymer, polypropylene/adhesive blend/aluminium, polypropylene/adhesive blend/steel, polypropylene/adhesive blend/glass, polypropylene/adhesive blend/wood, polypropylene/adhesive blend/leather, polypropylene/adhesive blend/nylon/adhesive blend/polypropylene, polypropylene/adhesive blend/EVOH/adhesive blend/polypropylene, and polypropylene/adhesive blend/aluminium/adhesive blend/polypropylene. Other metals, such as copper, steel and brass, can be used.

It is obvious that other combinations can be made by one skilled in the art using the principles and adhesive blends disclosed.

In preparing the adhesive blends used according to the invention from the above graft copolymers, elastomers and ethylene homopolymers or copolymers, any blending equipment or technique may, in principle, be used.

The composite structures according to the invention can be made by any of methods known to those skilled in the art for joining three or more elements together. In principle, these methods may be summarised as laminating the elements together under pressure. Specific methods which can be used, most of which are appropriate to elements in sheet form, are for example, blown film co-extrusion, cast film and sheet co-extrusion, blow moulding, co-extrusion, co-extrusion coating, powder coating, rotomoulding, profile co-extrusion, and wire coating co-extrusion.

In order that the invention may be more fully understood, the following Comparative Examples (not in accordance with the invention) and Invention Examples are given by way of illustration only.

For the purpose of the Comparative Examples and Invention Examples, adhesive blends were prepared in an electrically heated Brabender Plasticorder mixing head using a scroll type mixer under the following conditions: temperature — 400°F (204°C), rotor speed — 120 rpm, and mixing time — 10 min after flux.

The resulting blends were compression moulded into films 0.005—0.007 inch (0.13—0.18 mm) thick. The films were then heat sealed to the substrate under evaluation at an appropriate temperature and time. These conditions were:

1. Nylon 6 — 430°F (221°C), 2 sec.
2. Ethylene-vinyl alcohol copolymer (EVOH) — 430°F (221°C), 5 sec.
3. Polypropylene — 500°F (260°C), 5 sec.
4. Aluminium — 430°F (221°C), 2 sec.

The resultant composites were tested by cutting into strips one inch (2.54 cm) wide. Adhesion was then tested by a T-peel test similar to that described in ASTM D 187-72.

Comparative Example 1

X-methyl-bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic anhydride (XMNA) was reacted with a high density polyethylene homopolymer in a twin screw extruder to give a graft copolymer with 1.5 wt.% XMNA incorporation and a melt index of 1.5 g/10 min. The graft copolymer was blended in varying amounts with a random polypropylene-ethylene copolymer having a melt flow rate (MFR) of 2. These blends were heat sealed to nylon 6 for 2 sec at 430°F (221°C). T-peel adhesion results are summarized below.

Graft copolymer in blend (wt.%)	*Adhesion to nylon 6, lbs/in (kg/cm)*
3	0 (0)
5	0.3 (0.054)
7	0.6 (0.108)
10	0.0(0)

Comparative Example 2

Using the same graft copolymer as described in Comparative Example 1, blends were prepared with a propylene-ethylene block copolymer having an MFR of 2.

Graft copolymer in blend (wt.%)	*Adhesion to nylon 6, lbs/in (kg/cm)*
10	0.0 (0)
15	0.3 (0.054)
20	0.0 (0)

Comparative Example 3

The same blends used in Comparative Example 2 were heat s aled for 5 sec at 430°F (221°C) to an ethylene-vinyl alcohol copolymer (EVOH). All these blends gave extremely poor adhesion t EVOH. The samples could not be tested because they fell apart.

Comparative Example 4

Ninety percent of a propylene-ethylene block copolymer containing 7.8% ethylene was blended with 10 wt.% of the same graft copolymers as described in Comparative Example 1. This blend was heat sealed to EVOH and gave a heat seal adhesion of 0.5 lb/in (0.09 kg/cm).

Comparative Example 5

When 90% of a polypropylene homopolymer having an MFR of 4 blended with 10% of the same graft copolymer as described in Comparative Example 1, was heat sealed to EVOH, the resultant heat seal adhesion was 0.1 lb/in (0.018 kg/cm). When this same blend was heat sealed to a random polypropylene copolymer as described in Comparative Example 1, its adhesion was greater than 10 lbs/in (1.8 kg/cm).

The above Comparative examples show that if a polyethylene graft copolymer is blended with a polypropylene homopolymer or a random or a block copolymer containing ethylene, the adhesion to polar polymers is not satisfactory.

Invention Examples 1—7

Blends were prepared using a low density polyethylene (LDPE) with a melt index of 1.8 g/10 minutes, an ethylene-propylene-diene monomer terpolymer (EPDM) elastomer and the graft copolymer described in Comparative Example 1. These blends were tested for adhesion to an ethylene-vinyl alcohol copolymer (EVOH), a random polypropylene copolymer, aluminium and nylon 6. The results are shown in Table I below.

Table I

	Composition			Adhesion to			
	LDPE %	*EPDM %*	*Graft copolymer %*	*EVOH lb/in (kg/cm)*	*PP random copolymer lb/in (kg/cm)*	*Nylon 6 lb/in (kg/cm)*	*Aluminium lb/in (kg/cm)*
Example 1	90	—	10	>7.1 (>1.28)	0 (0)	4.4 (0.79)	5.4 (0.97)
2	65	25	10	>7.6 (>1.37)	0.5 (0.09)	—	—
3	60	30	10	>8.0 (>1.44)	2.8 (0.5)	>6.1 (>1.1)	4.1 (0.74)
4	50	40	10	>7.1 (>1.28)	>6.3 (>1.13)	>5.3 (>0.95)	5.9 (1.06)
5	45	45	10	>7.7 (>1.39)	>6.5 (>1.17)	>9.0 (>1.62)	5.3 (0.95)
6	35	55	10	>6.5 (>1.17)	>6.5 (>1.17)	—	—
7	25	65	10	7.4 (1.33)	>6.8 (>1.22)	>8.1 (>1.46)	—

These results show that if the blend contained at least 30% EPDM, adhesion was excellent not only to ethylene-vinyl alcohol copolymer, nylon 6 and aluminium, but also to polypropylene.

Invention Examples 8—12

Blends were prepared using the same low density polyethylene as described in Examples 1—7, the same graft copolymer described in Comparative Example 1, and a styrene-ethylene-butylene-styrene block copolymer (a styrene-hydrogenated diene-styrene copolymer known as Kraton G 1650 (SEBS)). The results of adhesion tests are shown below in Table II.

Table II

	Composition			Adhesion to			
	LDPE %	SEBS %	Graft copolymer %	EVOH lb/in (kg/cm)	PP random copolymer lb/in (kg/cm)	Nylon 6 lb/in (kg/cm)	Aluminium lb/in (kg/cm)
Example 8	65	25	10	6.7 (1.21)	1.1 (0.2)	>6.3 (>1.13)	—
9	60	30	10	6.8 (1.22)	5.5 (0.99)	>6.5 (>1.17)	7.7 (1.39)
10	45	45	10	5.7 (1.03)	>9.9 (>1.78)	3.7 (0.67)	3.7 (0.67)
11	35	55	10	5.6 (1.01)	>10.0 (>1.8)	>5.8 (>1.04)	—
12	25	65	10	7.4 (1.33)	>10.0 (>1.8)	>6.2 (>1.12)	—

Here again, the use of at least 30% of the elastomer enabled these blends to adhere to polypropylene in addition to adhering to ethylene-vinyl alcohol copolymer, nylon 6 and aluminium.

Invention Examples 13—15

Blends were prepared with a high density polyethylene having an MI of 0.8 and a density of 0.96+ with the same graft modified HDPE described in Comparative Example 1 and several elastomers: EPDM as described in Invention Examples 1—7, a styrene-ethylene-butylene-styrene block copolymer as described in Examples 8—12, and a polyisobutylene (PIB) (Vistanex L-80). The results in Table III show that blends containing 45% of the high density polyethylene, 45% of the elastomer and 10% of the modified high density graft copolymer gave good to excellent adhesion to all four substrates.

Table III

	Composition					Adhesion to			
	HDPE %	*EPDM* %	*PIB* %	*SEBS* %	*Graft copolymer* %	*Aluminium lb/in (kg/cm)*	*EVOH lb/in (kg/cm)*	*PP random copolymer lb/in (kg/cm)*	*Nylon 6 lb/in (kg/cm)*
Example 13	45	45			10	>6.8 (>1.22)	6.2 (1.12)	2.0 (0.36)	>8.7 (>1.57)
14	45	—	45		10	3.8 (0.68)	8.3 (1.49)	3.5 (0.63)	>7.3 (>1.31)
15	45	—	—	45	10	3.7 (0.67)	3.4 (0.61)	7.5 (1.35)	4.1 (0.74)
16	90	—	—	—	10	—	2.2 (0.4)	0.2 (0.04)	1.9 (0.34)

Glossary of terms

EVOH — ethylene-vinyl acetate copolymers
XMNA — X-methyl bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride
MFR — melt flow rate
HDPE — high density polyethylene
LDPE — low density polyethylene
EPDM — ethylene-propylene-diene monomer terpolymer
SEBS — styrene-ethylene-butylene-styrene copolymer known as Kraton G 1650
PIB — polyisobutylene

Claims

1. A composite structure comprising a polypropylene structure, a solid substrate and sandwiched therebetween, an adhesive blend comprising:

(a) from 0.1 to 95% by weight of a graft copolymer of from 70 to 99.999% by weight of a polyethylene backbone grafted with from 30 to 0.001% by weight of an unsaturated carboxylic acid or acid anhydride thereof,

(b) at least one elastomer which is a homopolymer or copolymer of isobutylene, a homopolymer of chloroprene, an elastomeric copolymer of ethylene and an α-olefin, a terpolymer of ethylene, an α-olefin and a diene, a random or block copolymer of a diene and a vinyl aromatic compound, a copolymer of a hydrogenated diene and a vinyl aromatic compound, a hydrogenated block copolymer of a diene and a vinyl aromatic compound, a butadiene homopolymer, chlorinated butyl rubber, neoprene, a styrene-ethylene-butylene-styrene block copolymer, or a copolymer of an ethylenically unsaturated nitrile and a diene, and

(c) an ethylene homopolymer and/or a copolymer of ethylene and an α-olefin.

2. A composite structure according to claim 1, in which, in component (a) of the adhesive blend, the polyethylene backbone polymer is a high density polyethylene having a density of 0.930 to 0.970.

3. A composite structure according to claim 2, in which the polyethylene backbone polymer has a density of 0.940 to 0.970.

4. A composite structure according to any of claims 1 to 3, in which, in component (a) of the adhesive blend, the carboxylic acid or anhydride is 4-methylcyclohex-4-ene-1,2-dicarboxylic acid anhydride, tetrahydrophthalic anhydride, x-methylbicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride, maleic anhydride, fumaric acid or acrylic acid.

5. A composite structure according to any of claims 1 to 4, in which component (c) of the adhesive blend is polyethylene having a density of 0.910 to 0.965.

6. A composite structure according to any of claims 1 to 4, in which component (c) of the adhesive blend is a copolymer of ethylene and an α-olefin containing 3 to 8 carbon atoms.

7. A composite structure according to any of claims 1 to 5, in which, in the adhesive blend, component (b) is polyisobutylene, chlorinated butyl rubber, neoprene or a styrene-ethylene-butylene-styrene block copolymer and component (c) is polyethylene.

8. A composite structure according to any of claims 1 to 7, in which the solid substrate is formed of a polar polymer, a metal, glass, paper, wood, leather or regenerated cellulose.

9. A composite structure according to any of claims 1 to 8, in which the solid substrate is formed of nylon or an ethylene-vinyl alcohol copolymer.

10. A composite structure according to any of claims 1 to 8, in which the solid substrate is formed of aluminium or steel.

11. A composite structure according to any of claims 1 to 10, which comprises polypropylene/adhesive blend/solid substrate/adhesive blend/polypropylene.

12. A method of making a composite structure according to any of claims 1 to 11, which comprises laminating the elements of the structure together under pressure.

13. A method of making a composite structure according to any of claims 1 to 11, which comprises laminating the elements of the structure together by co-extrusion.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1983. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained